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(54) Title: SIDE–CHAIN LIQUID CRYSTALLINE POLYMERS

(57) Abstract

Cholesteric polymer P1 obtainable by a ring–opening metathesis polymerization ("ROMP") of (a) from 10 to 50 mol–% of a monomer with the formula (I): $Z(B_1)_y$; (b) from 90 to 50 mol –% of (b1) from 0 to 100 mol –%, related to the sum of the amounts of (b1) and (b2), monomer with the formula (II): $Z(B_2)_y$; (b2) from 0–100 mol–%, related to the sum of (b1) and (b2), of a monomer with the formula (III): $Z(B_3)_y$; or a strained cyclic olefinic molecule, wherein at least one of the monomers (II) or (III) is present, the mol–percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol–%, three–dimensionally cross–linked cholesteric polymers P2, the corresponding monomers, processes for its preparations, uses and pigment compositions.

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Side-Chain Liquid Crystalline Polymers

The present invention relates to a cholesteric polymer P1 obtainable by a ring-opening metathesis polymerization ("ROMP") of strained cyclic olefins.

Further, the present invention relates to crosslinked cholesteric polymers, processes for the preparation of the inventive polymers and their use.

Schrock et al. describe in Macromolecules 25 (1992) 3609-3616 and 6586-6592 the synthesis and the ring-opening metathesis polymerization ("ROMP") of the norbornene monomer series 5-{[*n*-[(4´-methoxy-4-biphenylyl)oxy]alkyl]carbonyl}bicyclo[2.2.1]-hept-2-ene (1-*n*) with spacer lengths *n* of 2 to 8 and 9 to 12, resp., methylene units. The synthesized compounds contain an ester group bonded directly to the norbornene unit. Although the obtained polymers are side chain liquid crystalline polymers ("SCLCP"), they are neither crosslinkable nor do they show any cholesteric phases. In addition, the catalyst used is too sensible for industrial use.

Schrock et al. describe in Macromolecules 26 (1993) 1393-1401 further SCLCP which differ from those mentioned above as they contain an ether group bonded directly to the norbornene unit. The disclosed SCLCP, too, are not crosslinkable and they do not exhibit any cholesteric phases.

US 5,211,877 *inter alia* claims the use of three-dimensionally crosslinked, chiral, liquid crystalline polyorganosiloxanes as pigments. A drawback is the difficulty to control both the molecular weight and the polydispersity of the resulting polymers, unless they are not based on cyclosiloxanes (this is discussed in Macromolecules 25 (1992) p.3609, left col., 2nd paragraph). Another drawback is the laborious synthesis of the pigments.

US 5,362,315 claims a pigment whose color depends on the viewing angle. The pigment comprises oriented three-dimensionally support-free substances of liquid-crystalline structure having a chiral phase and, optionally dyes and pigments, wherein said optional dyes and pigments do not serve as a base for the oriented three-dimensionally crosslinked liquid-crystalline substances having a chiral phase.

WO 95/32247 describes interference pigments based on a SCLCP comprising a nematic and a chiral component. These pigments are synthesized e.g. by a in-situ photopolymerization of a nematic liquid crystalline diacrylate and a cholesteric liquid crystalline diacrylate, or a mixture of corresponding diacrylates and monoacrylates.

WO 96/02597 describes a process for printing substrates with a coating or printing agent, in which a mixture of mono- and/or diacrylates are polymerized, whereby at least one component is chiral.

WO 96/17901 describes a liquid crystalline material in the form of a cholesteric polymer network, wherein the polymerized material is obtainable by copolymerization of a compound having at least two equal polymerizable functional groups and a chiral polymerizable compound, the latter being a terpenoid. The crosslinking is carried out in-situ.

Hence, the object of this invention was to provide side-chain liquid crystalline polymers which are obtainable by a ring-opening metathesis polymerization of strained cyclic rings whereby the inventive compounds and the processes for its preparations should not show the abovementioned drawbacks. Especially, the inventive polymers should be cholesteric, crosslinkable, should show a narrow polydispersity, and the crosslinking of the cholesteric polymers should be carried out easily with regard to a technical and economical process.

Accordingly, a cholesteric polymer P1 was found obtainable by a ring-opening metathesis polymerization ("ROMP") of

(a) from 10 to 50 mol-% of a monomer with the formula I

$$Z(B_1)_y \qquad I$$

(b) from 90 to 50 mol-% of

(b1) from 0 to 100 mol-%, related to the sum of the amounts of (b1) and (b2), monomer with the formula II

$$Z(B_2)_y \qquad II$$

(b2) from 0 to 100 mol-%, related to the sum of (b1) and (b2), of a monomer with the formula III

$$Z(B_3)_y \qquad III$$

or a strained cyclic olefinic molecule,

wherein at least one of the monomers II or III is present,

the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%, wherein

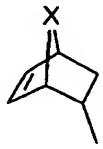
Z stands for A_1-A_2-A_3-A_4-A_5-A_6-A_7-, if y is 1, or, in case y is 2, for A_1-(A_2-A_3-A_4-A_5-A_6-A_7-)$_2$

B_1 stands for a chiral organic group,

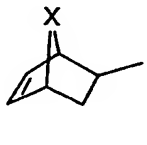
B_2 stands for an organic crosslinkable group,

B_3 stands for an organic, non-chiral, non-crosslinkable group,

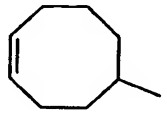
A_1 stands for a radical selected from the group consisting of



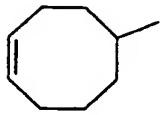
IVa



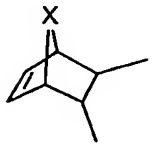
IVb



Va



Vb



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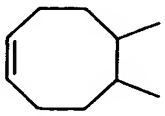


VIa VIb

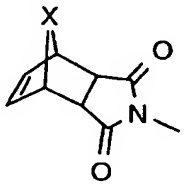
including the exo- and the endo-isomers of the radicals IVa, IVb, and VIa, and whereby y is 1 in case A_1 is a monomer selected of IVa, IVb, Va, or Vb, or y is 2 in case A_1 is one of the biradicals VIa or VIb, and in which

X is selected from the group consisting of -CH_2-, -O- and -S-

A_2 is -CH_2- or -C(O)-

A_3 is -O- or -NH-, or

A_1-A_2-A_3 stands for a radical of the formula VII



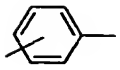
VII

A_4 is -$(CH_2)_{x1}$- or -$[CH_2$-CH_2-O-$]_{x2}$-CH_2-CH_2-, wherein x_1 is an integer from 2 to 20, and x_2 is an integer from 1 to 6,

A_5 is one of the following radicals

-O-, -S-, -CO-O-, -O-CO-, -NH-CO-, -CO-NH-, -NH-

A_6 is



A_7 is -CO-O-, -O-CO-, -NH-CO-, -CO-NH-.

Further, a three-dimensionally crosslinked, cholesteric polymer P2, the corresponding monomers, processes for the preparation of the inventive polymers and monomers, and their uses were found.

According to the invention on hand, the cholesteric polymer P1 is obtainable by a ROMP-reaction of

(a) from 10 to 50, preferred from 20 to 50 mol-% of a monomer with the formula I

$$Z(B_1)_y \qquad I$$

(b) from 90 to 50, preferred from 80 to 50 mol-% of

(b1) from 0 to 100, preferred from 20 to 100 mol-%, related to the sum of the amounts of (b1) and (b2), monomer with the formula II

$$Z(B_2)_y \qquad II$$

(b2) from 100 to 0, preferred from 80 to 0 mol-%, related to the sum of (b1) and (b2), of a monomer with the formula III

$$Z(B_3)_y \qquad III$$

or a strained cyclic olefinic molecule,

wherein at least one of the monomers II or III is present,

the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%, wherein

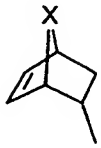
Z stands for A_1-A_2-A_3-A_4-A_5-A_6-A_7-, if y is 1, or, in case y is 2, for A_1-(A_2-A_3-A_4-A_5-A_6-A_7-)$_2$

B_1 stands for a chiral organic group,

B_2 stands for an organic crosslinkable group,

B_3 stands for an organic, non-chiral, non-crosslinkable group,

A_1 stands for a radical selected from the group consisting of



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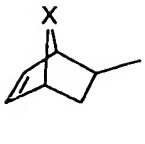

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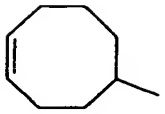
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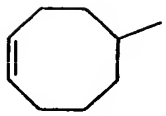
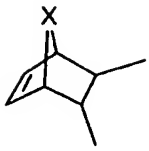

,

IVa IVb Va Vb



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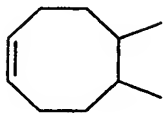


VIa VIb

whereby the exo- and the endo-isomers of the radicals IVa, IVb, and VIa, where possible, are included, and whereby y is 1 in case A_1 is a monomer selected of IVa, IVb, Va, or

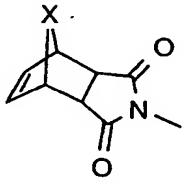
Vb, and y is 2 in case A_1 is one of the biradicals VIa or VIb, and in which

X is selected from the group consisting of $-CH_2-$, -O- and -S-, preferably, $-CH_2-$,

A_2 is $-CH_2-$ or -C(O)-,

A_3 is -O- or -NH-, preferably -O-, or

A_1-A_2-A_3 stands for a radical of the formula VII



VII

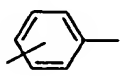
X being preferably $-CH_2-$,

A_4 is $-(CH_2)_{x1}-$ or $-[CH_2-CH_2-O-]_{x2}-CH_2-CH_2-$, wherein x_1 is an integer from 2 to 20, preferably from 4 to 10 such as 4, 5, 6, 7, 8, 9 and 10, and x_2 is an integer from 1 to 6 like 1, 2, 3, 4, 5, or 6, preferably 1, 2 or 3,

A_5 is one of the following radicals

-O-, -S-, -CO-O-, -O-CO-, -NH-CO-, -CO-NH-, or -NH-

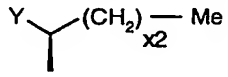
A_6 is



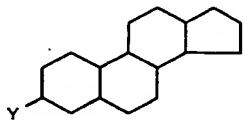
A_7 is -CO-O-, -O-CO-, -NH-CO-, or -CO-NH-.

As chiral organic group B_1 usually any organic group exhibiting chirality, i.e. a molecule having at least a center of chirality or being intrinsically asymmetric, can be chosen. Such molecules and methods for the synthesis of chiral compounds are well-known in the art and examples can be found in every case-book dealing with organic chemistry.

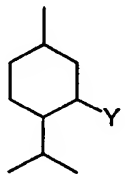
Preferred groups B_1 are e.g. chiral hydrocarbons such as

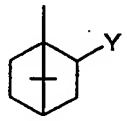


with Y being a single bond to A_7,
steroid radicals



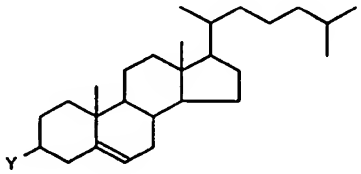
such as perhydro-cyclopenta[a]phenanthren (gonane), preferably cholestane, particularly preferred cholesteryl radicals,
terpenoid radicals





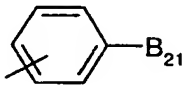
such as menthyl or camphor radicals,
alkaloid radicals such as quinine, groups which are derived from sugars, binaphthyl- or binaphthyl-derivatives, optically active glycoles, dialcohols or aminoacids. Such compounds are well known to the chemist and e.g. described in WO 96/02597, WO 95/32247.

Particularly preferred organic chiral radicals are derivatives of e.g. cholesteryl radicals ("chol"), preferably



terpenoid radicals such as methyl or camphor radicals, and alkaloid radicals such as quinine.

As organic crosslinkable group B_2, a radical of the formula



wherein B_{21} stands for an unsaturated group, preferably an unsaturated group having at least one carbon-carbon double bond, particularly preferred B_{21} comprises the vinyl group. E.g. B_{21} stands preferably for CH_2=C(H)-C(O)-O-, CH_2=C(Me)-C(O)-O-, the corresponding amides CH_2=C(H)-C(O)-NH-, CH_2=C(Me)-C(O)-NH-, most preferred CH_2=C(Me)-C(O)-NH-.

As organic, non-chiral, non-crosslinkable group B_3, preferably

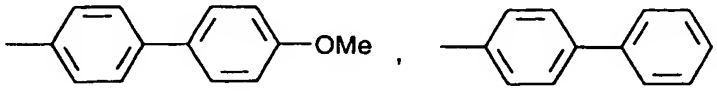
wherein R_1 stands for hydrogen, C_1-C_{10}-alkyl, C_1-C_{10}-alkoxy, C_1-C_{10}-alkylmercapto, -CN, -NO_2 or halogen, can be used.

C_1-C_{10}alkyl stands for e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, i-butyl, tert.-butyl, n-amyl, tert.-amyl, hexyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, preferably for C_1-C_4alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, i-butyl, tert.-butyl;

C_1-C_{10}-alkoxy stands for e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, i-butoxy, tert.-butoxy, n-amyloxy, tert.-amyloxy, hexyloxy, heptyloxy, octyloxy, 2-ethylhexyloxy, nonyloxy, decyloxy, preferably for C_1-C_4alkoxy such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.-butoxy, i-butoxy, tert.-butoxy;

C_1-C_{10}-alkylmercapto stands for e.g. methylmercapto, ethylmercapto, n-propylmercapto, isopropylmercapto, n-butylmercapto, sec.-butylmercapto, i-butylmercapto, tert.-butylmercapto, n-amylmercapto, tert.-amylmercapto, hexylmercapto, heptylmercapto, octylmercapto, 2-ethylhexylmercapto, nonylmercapto, decylmercapto, preferably for C_1-C_4alkyl such as methylmercapto, ethylmercapto, n-propylmercapto, isopropylmercapto, n-butylmercapto, sec.-butylmercapto, i-butylmercapto, tert.-butyl;

Preferred non-crosslinkable, non-chiral organic groups B_3 are e.g.

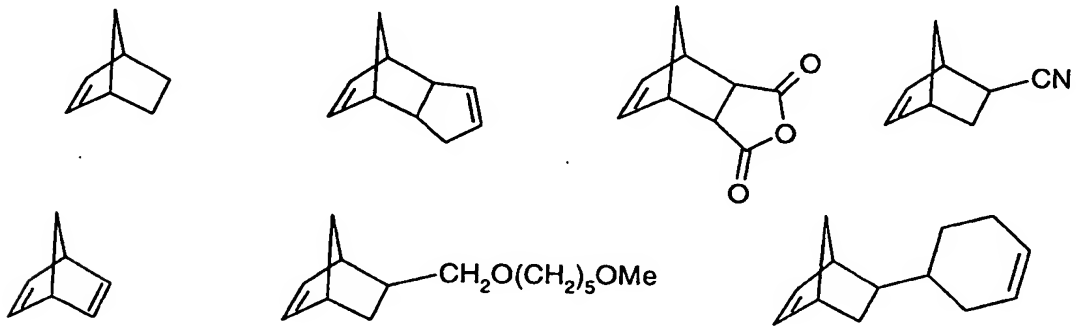


In a further preferred embodiment of the present invention strained cyclic olefinic molecules are used as monomer III, whereby strained cyclic olefinic molecules has the meaning within the scope of this invention that all cycloolefines can be used, with the exception of cyclohexene and its derivatives which can not be polymerized by a ring opening metathesis reaction.

E.g. strained cyclic olefinic molecules can be monocyclic or polycyclic, bridged or non-bridged ring systems, preferably with two to four rings, which can be unsubstituted or substituted, and which can contain one or more hetero atoms such as O, S, N or Si, in one or more rings, and which can contain condensed aromatic or heteroaromatic rings like o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. Preferably the single cyclic rings contain 3 to 16, more preferably from 3 to 12, most preferred 3 to 8 carbon or hetero atoms. The strained cyclic olefinic molecules can contain further non-aromatic double bonds, depending on the size of the ring, preferably between two to four additional double bonds.

If the strained cyclic olefinic molecules do contain more than one double bond, e.g. 2 to 4 double bonds, then, usually depending on the chosen conditions of the reaction, the chosen monomer and the amount of the catalyst, three-dimensionally crosslinked polymers can be built.

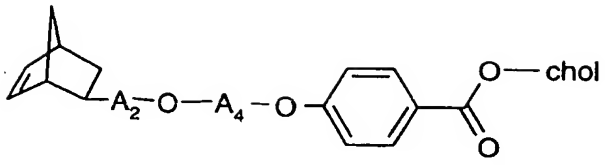
Preferred cycloolefinic molecules are Diels-Alder-adducts of cyclopentadiene such as e.g.

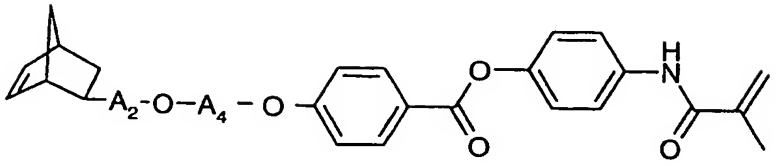


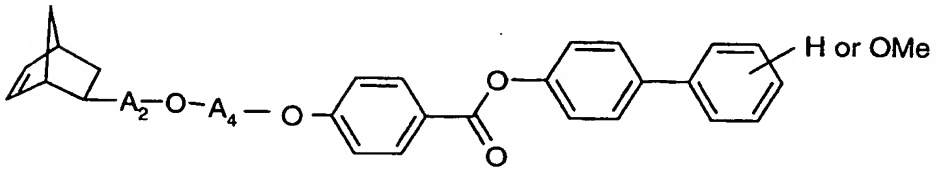
whereby, norbornene and dicyclopentadiene are most preferred.

Such strained cyclic olefinic molecules are commercially available or can be synthesized according to well-known methods.

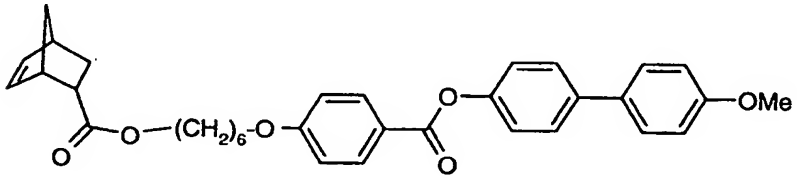
Preferred cholesteric polymers P1 are obtainable by the polymerization of e.g.

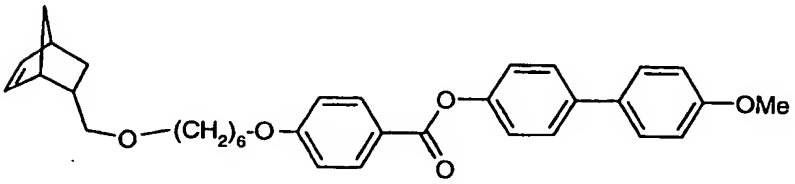


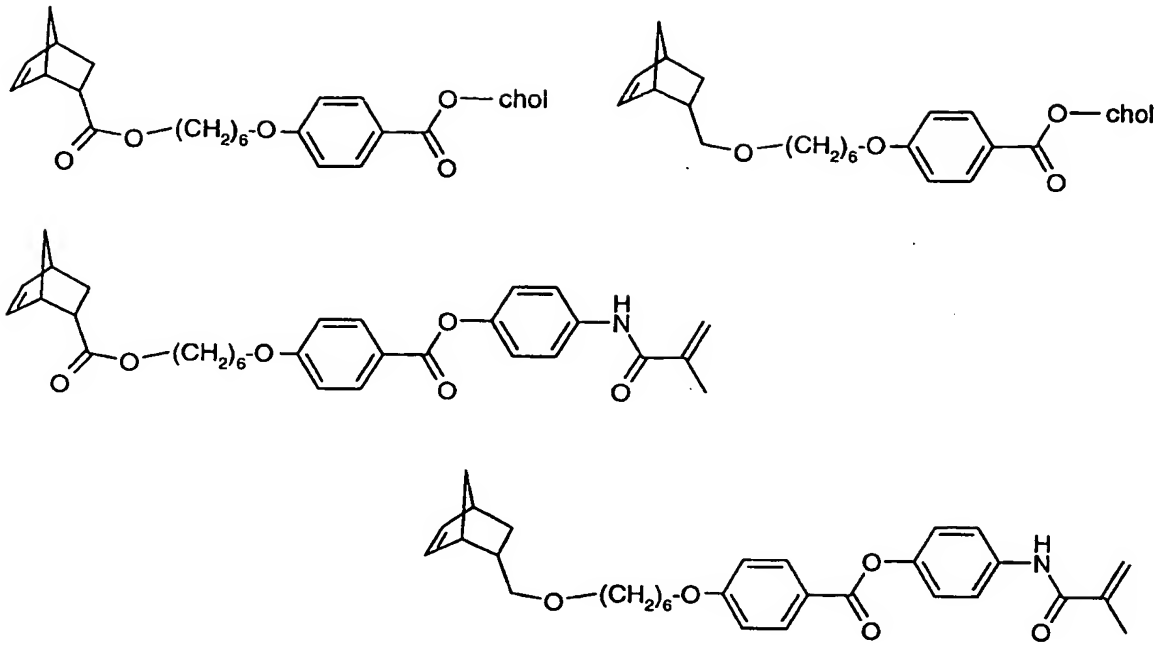




Most preferred cholesteric polymers P1 are obtainable by the polymerization of e.g.







The corresponding inventive monomers I, II and III can be synthesized by methods well known in the art. In a preferred embodiment $Z\text{-}B_1$, $Z\text{-}B_2$ and $Z\text{-}B_3$ can be obtained via two routes, if A_1 is a radical of formula IV (a or b) or V (a or b), and depending on whether A_2 is $-CH_2-$ or -CO-, and A_3 stands for -O-. The first route, (I), in which A_2 is $-CH_2-$, A_5 is -O- and A_7 is -COOH, comprises the following steps:

(I) $A_1\text{-}CH_2\text{-}OH + Hal\text{-}A_4\text{-}Hal \longrightarrow A_1\text{-}CH_2\text{-}O\text{-}A_4\text{-}Hal$ (1)

VIII IX X

$A_1\text{-}CH_2\text{-}O\text{-}A_4\text{-}Hal + H\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H \longrightarrow A_1\text{-}CH_2\text{-}O\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H$ (2)

XI XII

$A_1\text{-}CH_2\text{-}O\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H + B_{1,2,3}OH \longrightarrow A_1\text{-}CH_2\text{-}O\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}B_{1,2,3}$ (3)

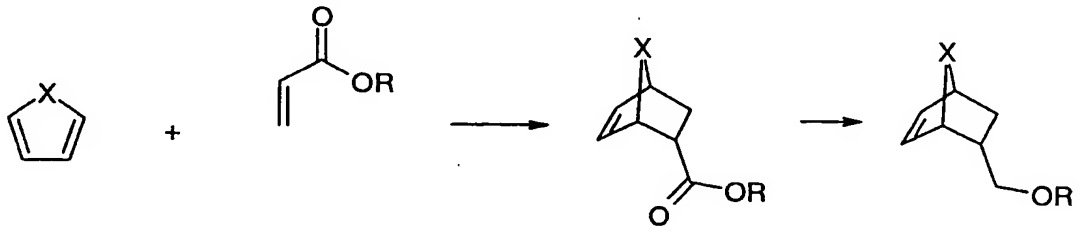
XIII

wherein $B_{1,2,3}$ means B_1 or B_2 or B_3.

Compound VIII, $A_1\text{-}CH_2\text{-}OH$, is known or can be prepared by well known methods. E.g.,

if A_1 stands for the norbornene radical and the bridging group X is $-CH_2-$, then this compound, bicyclo[2.2.1]hept-5-ene-2-methanol, is known e.g. from Macromolecules 26 (1993) 1393-1401. Usually, one can chose either the endo- or exo-derivative, preferably one choses a ratio endo/exo in the range of 5:1 to 20:1, more preferably 8:1 to 10:1, particularly preferred 9:1.

If A_1 stands for the norbornene radical and X is -S- or -O-, then compound VIII can be synthesized according to the following route:



Corresponding cyclooctene compounds as starting materials are known, e.g.

the first compound is known from Beilstein, EIV, Vol. 9, p.142-143, the second one has the CAS-registration number 13366-81-9.

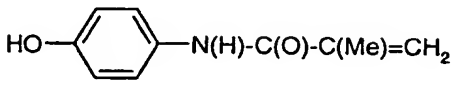
Compound IX, Hal-A_4-Hal, preferably Hal stands for Cl, Br, or I, e.g. is commercially available from Fluka.

Reaction step (I)(1) e.g. can be carried out analogously to the method described in Macromolecules 26 (1993) 1393-1401.

Compounds of the formulae XI, H-A_5-A_6-A_7-H, are well known in the art, commercially available, like e.g. o-, m-, or p-hydroxy-benzoic acid, and/or can be prepared by known methods.

Reaction step (I)(2) is a simple nucleophilic displacement, well known in the art (see e.g. "Methoden der Organischen Chemie", Houben-Weyl, vol. 6/3, chapter "Methods for the preparation and conversion of ethers", 4th edition, 1965, p.24-32.

Compounds of the formulae XIII, $B_{1,2,3}OH$, like B_1OH and B_2OH are commercially available, and B_3OH, e.g. as



is known from e.g. from J.Org.Chem. USSR 4(1968) 802.

Reaction step (I)(3) is a usual esterification and can be carried out according to known methods.

If compound XII is a carboxylic acid, then it is preferred to build the corresponding acid chloride thereof in a first step, and, in a second step, the acid chloride is reacted with the alcohol XIII to yield the corresponding ester. Such a reaction is well-known to the organic chemist, e.g. such a reaction is described in detail in Methoden der Organischen Chemie, Houben-Weyl, "Carbonsäuren und Derivate", E5, 4th Ed., esp. p. 695-700. Another possibility is to use the so-called "DCC"-method (DCC stands for dicyclohexylcarbodiimide), described in Methoden der Organischen Chemie, Houben-Weyl, "Carbonsäuren und Derivate", E5, 4th Ed., 1985, p. 674 to 676.

A second route, (II), to synthesize the starting monomers I, II and III, in which A_1 is a radical of formula IV or V, A_2 is -CO- and A_3 and A_5 stand for -O-, and A^7 stands for -C(O)-O-, comprises the following steps:

(II) $H\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H$ (XI) + $HO\text{-}A_4\text{-}Hal$ (XIV) ----> $HO\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H$ (XV) (4)

$HO\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H$ + $A_1\text{-}COOH$ (XVI) ----> $A_1\text{-}COO\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A^7\text{-}H$ (XVII) (5)

$A_1\text{-}COO\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}H$ + $B_{1,2,3}OH$ ----> $A_1\text{-}COO\text{-}A_4\text{-}A_5\text{-}A_6\text{-}A_7\text{-}B_{1,2,3}$ (6)

Compound XIV, $HO\text{-}A_4\text{-}Hal$, in which Hal preferably stands for Cl, Br, or I is commercially available.

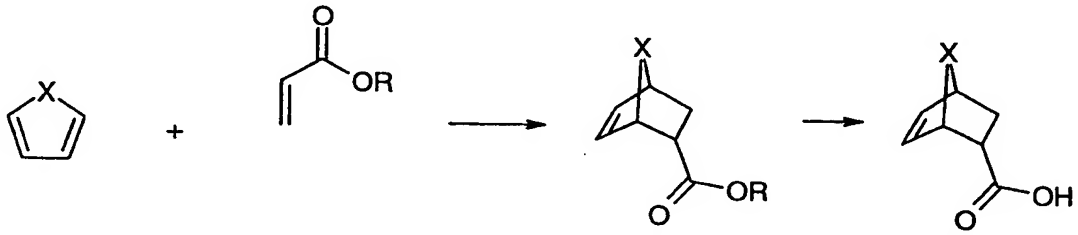
Reaction step (II)(4) can be carried out in analogy to the method described in Macromolecules 28 (1995) 806.

Compounds of formulae XVI, A_1-COOH are commercially available or can be prepared according to known methods.

E.g., if A_1 stands for the norbomene radical and the bridging group X is -CH_2-, then this compound, bicyclo[2.2.1]hept-5-ene-2-carboxylic acid, is commercially available from Aldrich or can be prepared starting from cyclopentadiene with acrylic acid methyl ester yielding the corresponding bicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester, which can be hydrolyzed into the carboxylic acid by known methods.

Usually, one can chose either the endo- or exo-derivative, preferably one choses a ratio endo/exo in the range of 5:1 to 20:1, more preferably 8:1 to 10:1, particularly preferred 9:1.

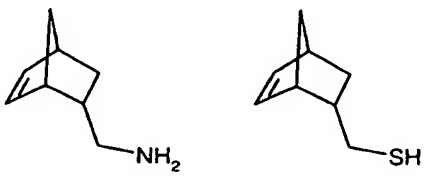
If A_1 stands for the norbornene radical and the bridging group X is -S- or -O-, then the norbornene derivative can be prepared via a Diels-Alder reaction followed by a hydrolysis step:



Reaction step (II)(5) is a usual esterification and can be carried as described above (compound esterification of compound XII) via an acid chloride or via the DCC-method.

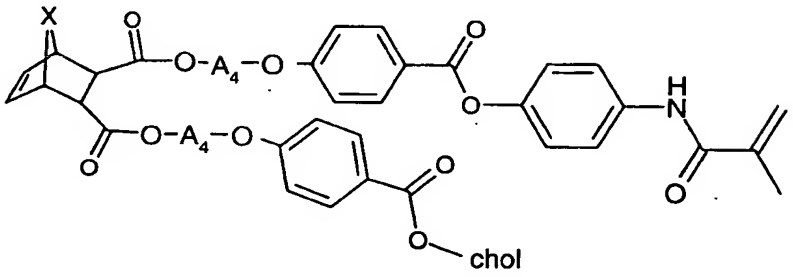
Reaction step (II)(6), too, is a usual esterification and can be carried as described above (compound esterification of compound XII) via an acid chloride or via the DCC-method.

Compounds of the formula VIa and VIb are also commercially available or can be prepared to well known methods. E.g. 5-norbornene-2,3-dicarboxylic acid is commercially available from Aldrich, the amino derivative

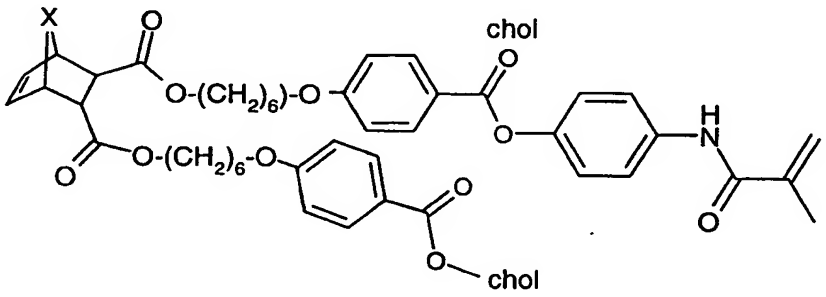


is known from Beilstein EIII, vol. 12, p. 213, and the corresponding thiol is registered under CAS 81237-92-5.

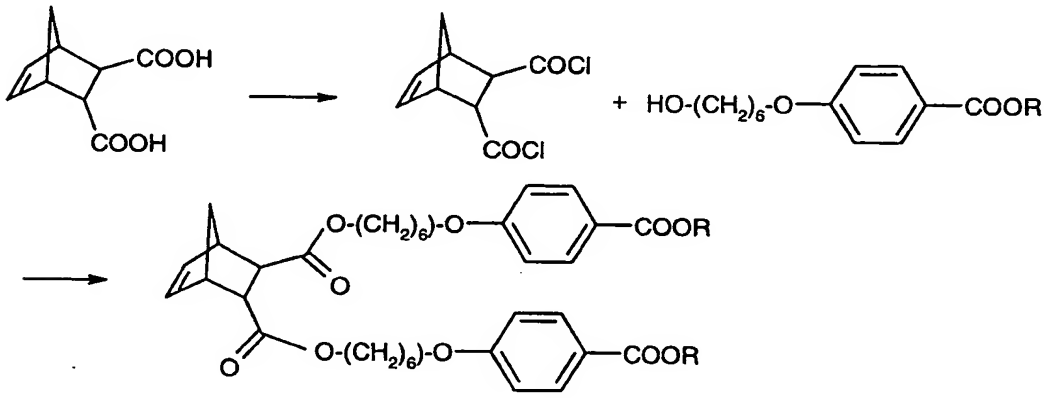
Preferred monomers of formula VI, especially of formula VIa, are e.g.



most preferred is the following inventive monomer

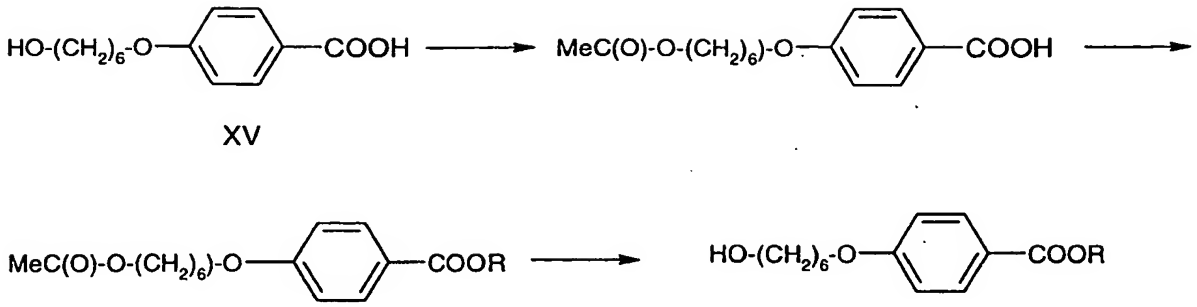


Monomers on the basis of compounds VIa can be synthesized according to known methods, e.g. via the following route:



whereby the acid chloride can be prepared e.g. with thionyl chloride, and the esterification can be carried out e.g. in analogy to the abovementioned possibilities or in the presence of a base such as triethylamine in tetrahydrofurane.

The ester can be prepared starting from a compound with the formula XV, which is converted into an ester e.g. with the known thionyl chloride route, whereby the alcohol group is preferably protected during esterification:



XV

Hence, another embodiment of the instant invention relates to inventive monomers Z-B_1, Z-B_2 and Z-B_3.

A further embodiment of the instant invention relates to a composition comprising from (a) 10 to 50 mol-% of compound $Z(B_1)_y$ and (b) from 90 to 50 mol-% of a mixture of (b1) from 0 to 100 mol-% of compound $Z(B_2)_y$ and (b2) from 100 to 0 mol-% $Z(B_3)_y$, wherein the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%.

Another embodiment of the present invention relates to three-dimensionally crosslinked cholesteric polymers P2, whereby the inventive cholesteric polymers P1, in which the amount of Z-B_2, II, is not 0, are further treated by crosslinking the crosslinkable groups B_2 in a photo polymerization reaction or thermally induced, preferably by a photo polymerization.

Therefore, in a preferred embodiment of the present invention inventive polymers P1 are used, which have been prepared starting with amounts of Z-B_1 in the range of from 10 to 50, preferably from 20 to 50 mol-%, and 90 to 50, preferably 80 to 50 mol-% of a mixture of from 0 to 100, preferably 20 to 100 mol-% Z-B_2 and 100 to 0, preferably from 80 to 0 mol-% Z-B_3, y being preferably 1.

The polymer properties of the cholesteric polymers P1 usually depend on essentially the chosen educts (monomers), process parameters, and the desired properties. E.g. the molecular weight can be chosen in a range of from 5,000 to 100,000, preferably 10,000-40,000 g/mol, the polydispersity is - as a rule - low, and preferably is in the range of from 1.0 to 2.0, particularly preferred from 1.1 to 1.5. It is further preferred to chose the T_g in the range of 70 to 200, more prefereably from 70 to 150°C.
Another embodiment of the present invention relates to a process for the preparation of the inventive polymers P1, wherein the polymerized material is obtainable by copolymerization of

at least two kinds of monomers, wherein one monomer is a chiral compound, characterized in

carrying out the copolymerization by a ring opening metathesis polymerization in the presence of a catalyst of

(a) from 10 to 50, preferred from 20 to 50 mol-% of a monomer with the formula I

$$Z(B_1)_y \qquad I$$

(b) from 90 to 50, preferred from 80 to 50 mol-% of

(b1) from 0 to 100, preferred from 20 to 100 mol-%, related to the sum of the amounts of (b1) and (b2), monomer with the formula II

$$Z(B_2)_y \qquad II$$

(b2) from 0 to 100, preferred from 80 to 0 mol-%, related to the sum of (b1) and (b2), of a monomer with the formula III

$$Z(B_3)_y \qquad III$$

or a strained cyclic olefinic molecule,

wherein at least one of the monomers II or III is present,

the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%.

Usually the reaction temperature is chosen in the range of from 0 to 110, preferably from 20 to 80°C.

Generally, the reaction pressure is chosen in the range of from 80 to 500, preferably from 90 to 200 kPa.

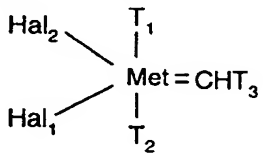
Preferably, the reaction time is chosen in the range of from 1 to 24, preferably from 3 to 10 h.

As catalysts usually all known catalysts which are able to catalyze a ring opening metathesis reaction can be used.

Such polymerization catalysts are well-known e.g. from US 4,426,502, EP-A 348,852, WO 96/20235, WO 93/20111, WO 96/04289, WO 97/06185.

Preferred catalysts are described e.g. by Schrock e.g. in Macromolecules 25 (1992) 3609-3616. Those catalysts are of the type $Mo(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$, $Mo(CHR)(NAr)(OC(Me)(CF_3)_2)_2$ (Ar = 2,6-C_6H_3-i-Pr_2, R = t-Bu or CMe_2Ph).

Other preferred catalysts are based on Ruthenium or Osmium such as



wherein Met stands for Ru or Os,
Hal_1 and Hal_2 denote independently from each other halogen such as F, Cl, Br or I,
T_1 and T_2 denote independently from each other for a tertiary phosphine or phosphite, or both together stand for a bitertiary diphosphine or diphosphite,
T_3 stands for an organic group such as aryl, alkyl, alkenyl, vinyl, benzyl, or a heteroatom bonded group such as alkoxy, aryloxy, alkenyloxy, alkylthio or arylthio.

Mostly preferred catalysts are e.g. $Cl_2[P(i\text{-}Pr)_3]_2Ru{=}CHPh$, $Cl_2[P(cyclohexyl)_3]_2Ru{=}CHPh$, e.g. described in WO 96/04289 and WO 97/06185.

Preferably, the mol ratio of catalyst to the total amount of monomers is chosen in the range of from 0.0005 to 0.1, preferably from 0.01 to 0.04.

If desired, the above described processes can be carried out in the presence of a solvent such as - usually depending on the chosen catalyst - halogenated hydrocarbons like methylene chloride, 1,1,2-trichloroethane, and chloroform, aromatic hydrocarbons like toluene and xylenes.

Usually the amount of solvent is chosen in the range of from 0.01 mol to 1 mol per 1 liter, preferred 0.08 to 0.12, particularly preferred 0.1 mol/l of the reaction mixture.

Another preferred embodiment of this invention relates to the abovementioned processes, whereby at the end of the reaction a catalyst end-capping agent is added to remove the catalyst from the polymer chain.

Such a catalyst end-capping agent can be either a vinyl compound such as vinyl ethyl ether, vinyl trimethyl silane for the ruthenium based catalysts, or an aldehyde such as benzaldehyde for the molybdenum based catalysts. Such compounds are described e.g. in Organometallics 12 (1993) 759 and J.Am.Chem.Soc. 118 (1996), 100.

In general, the mol ratio of the catalyst end capping agent to the amount of used catalyst is chosen in the range of from 1:1 to 1:1000, preferred from 1:10 to 1:100.

As a rule the reaction mixture can be worked up in a known manner. Preferably, the polymer is precipitated in a solvent, in which the polymer is not or only partially soluble, such as ethanol or methanol.

If desired, chain transfer agents such as terminal alkenes can be added to the reaction mixture. Such agents are known, e.g. from Macromolecules 28 (1995) 500-511, esp. for molybdenum based catalysts, and from Macromolecules 26 (1993) 4742-4747 for ruthenium based catalysts.

Another embodiment of the instant invention relates to a process for the preparation of the crosslinked polymer P2, wherein the inventive cholesteric polymer P1 (wherein the preparation step the amount of component (b1) has been chosen to be greater than zero, is further treated by crosslinking the crosslinkable groups B_2 in a photo polymerization reaction or thermally induced, preferably by a photo polymerization.

In a preferred embodiment, the polymeric material usually is crosslinked in such a manner that it is applied at a sufficient temperature, depending on the kind of used polymeric material, e.g. - in case of norborneethers and norborneesters are used - of from 0 to 180°C, preferably 20 to 120°C, to a substrate, e.g. made out of a polyester, then oriented by conventional methods, for example, by treating the melt with a doctor blade or by applying electrical or magnetic fields and, subsequently, exposing the whole composition to radiation from a UV lamp.

Preferably the polymeric material is crosslinked in the presence of a photoinitiator, a polymerization inhibitor, and, if desired, non-mesogenic monomers, and/or a reactive diluter, and/or a chiral dopant.

Usually, the layer thickness is chosen in the range of from 3 to 24, preferably of from 3 to 6 μm.

In a particularly preferred embodiment, a photoinitiator is added to the polymeric material (such as the known QUANTACURE ®, or IRGACURE® type photoinitiator types) in an effective amount. The use of such a photoinitiator is described in more detail for example in US 5,211,877.

The crosslinking can also be carried out by known methods using heat, i.e. thermally induced.

As a rule, as polymerization inhibitors dihydroxy benzene, which can be substituted with C_1-C_6-alkyl or in which one or both hydroxy groups are replaced with an ether group. Such compounds are described e.g. in US 5,211,877. Preferred compounds are e.g. hydroquinone, hydroquinone mono methylether, 4-tert.-butyl catechol.

If desired, a chiral dopant such as cholesteryl-4-methacryloyloxy-benzoate (see e.g. US 5,211,877) can be applied in amounts in the range of from 5 to 40% by weight, related to the amount of polymer P1.

If desired, a reactive diluter such as a dimethacrylate, e.g. ethanedioldimethacrylate, diethyleneglycoldimethacrylate, triethyleneglycoldimethacrylate, or hexanedioldimethacrylate can be applied in amounts in the range from 0.1 to 20 % by weight, related to the amount of P1.

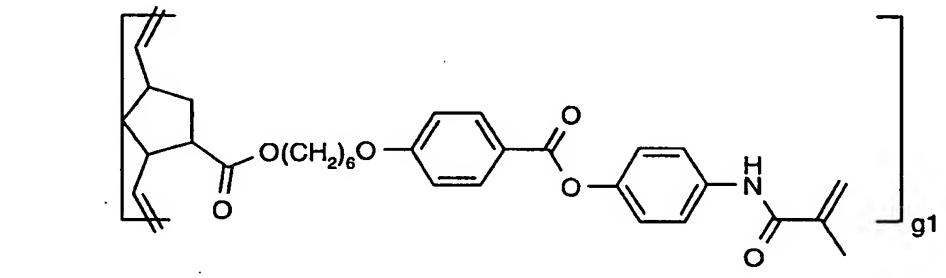
In case the crosslinking is carried out photochemically, the photoinitiator generally is chosen in an amount in the range of 0.1 to 3% b.w., based on the polymer P1, the polymerization inhibitor generally is chosen in an amount in the range of from 0.01 to 0.05% b.w., based on the polymer P1, the amount of diluter generally is chosen in the range of from 0.1 to 20% b.w., based on the polymer P1.

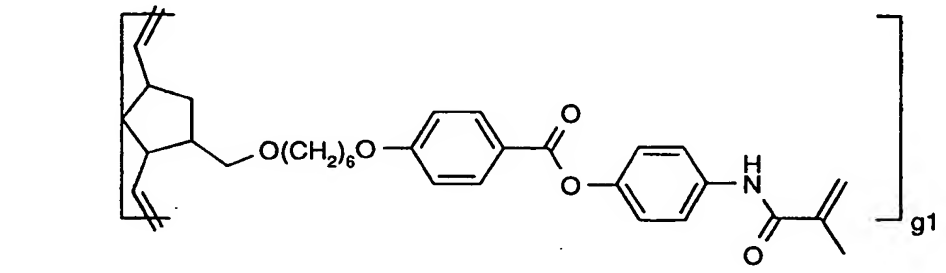
Usually, the crosslinking is carried out with UV light having a wavelength in the range of from 200 to 240 nm for a time period generally in the range of from 10 to 60 seconds depending on the chosen power.

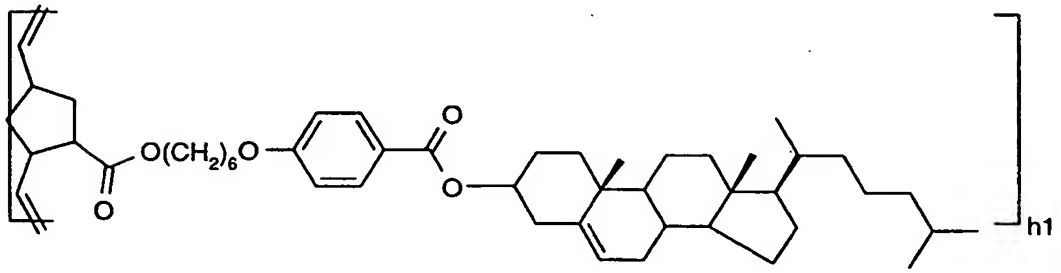
After the crosslinking, the obtained polymer P2 generally is removed mechanically by peeling off the support by known methods, e.g. by guiding the backing over a deflecting roller of small diameter, or using a ultrasonic bath. However, any other method by which the polymerized material can be removed from the backing is also suitable.

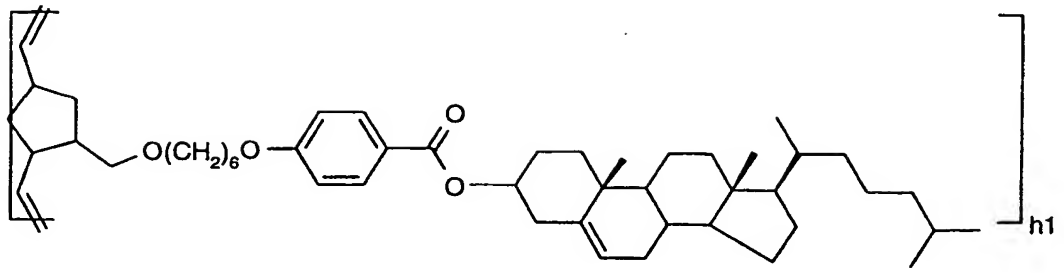
To obtain flakes, the pigment material usually can be milled in a known manner, for example using a mill, such as an air-jet mill.

Particularly preferred crosslinked side-chain liquid crystalline polymers P2 are those comprising as repeating units the following structures









wherein g1 = 1 - h1, and g1 is usually in the range of from 10 to 90, preferred 20 to 80 mol-%, related to the sum of g1 and h1, and wherein A_2-A_3 are either an ether group or an ester group.

Another embodiment of the present invention is related to the use of the inventive polymers P1 as precursor for the preparation of the inventive compounds P2, whereby P1 is crosslinked by the above described methods.

Another embodiment of the present invention relates to the use of the inventive polymer P2 as pigments for coloring high molecular weight organic materials, e.g. biopolymers, plastic materials, including fibres, glasses, ceramic products, for formulations in decorative cosmetics, for the preparation of inks, printing inks, paint systems, in particular automotive paints and dispersion colors.

Illustrative examples of suitable organic materials of high molecular weight which can be colored with the inventive polymer P2 of this invention are vinyl polymers, for example polystyrene, poly-α-methylstyrene, poly-p-methylstyrene, poly-p-hydroxystyrene, poly-p-hydroxyphenylstyrene, polymethyl methacrylate and polyacrylamide as well as the corresponding methacrylic compounds, polymethylmaleate, polyacrylonitrile, polymethacrylonitrile, polyvinyl chloride, polyvinyl fluoride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl acetate, polymethyl vinyl ether and polybutyl vinyl ether; polymers which are derived from maleinimide and/or maleic anhydride, such as copolymers of maleic anhydride with styrene; polyvinyl pyrrolidone; ABS; ASA; polyamides; polyimides; polyamidimides; polysulfones; polyether sulfones; polyphenylene oxides; polyurethanes; polyureas; polycarbonates; polyarylenes; polyarylene sulfides; polyepoxides; polyolefins such as polyethylene and polypropylene; polyalkadienes; biopolymers and the derivatives thereof e.g. cellulose, cellulose ethers and esters such as ethylcellulose, nitrocellulose, cellulose acetate and cellulose butyrate, starch, chitin, chitosan, gelatine, zein; natural resins; synthetic resins such as alkyd resins, acrylic resins, phenolic resins, epoxide resins, aminoformaldehyde resins

such as urea/formaldehyde resins and melamine/formaldehyde resin; vulcanized rubber; casein; silicone and silicone resins; rubber, chlorinated rubber; and also polymers which are used, for example, as binders in paint systems, such as novolaks which are derived from C_1-C_6-aldehydes such as formaldehyde and acetaldehyde and a binucluear or mononuclear, preferably mononuclear, phenol which, if desired, is substituted by one or two C_1-C_9alkyl groups, one or two halogen atoms or one phenyl ring, such as o-, m- or p-cresol, xylene, p-tert-butylphenol, o-, m- or p-nonylphenol, p-chlorophenol or p-phenylphenol, or a compound having more than one phenolic group such as resorcinol, bis(4-hydroxyphenyl)methane or 2,2-bis(4-hydroxyphenyl)propane; as well as suitable mixtures of said materials.

Particularly preferred high molecular weight organic materials, in particular for the preparation of a paint system, a printing ink or ink, are, for example, cellulose ethers and esters, e.g. ethylcellulose, nitrocellulose, cellulose acetate and cellulose butyrate, natural resins or synthetic resins (polymerization or condensation resins) such as aminoplasts, in particular urea/formaldehyde and melamine/formaldehyde resins, alkyd resins, phenolic plastics, polycarbonates, polyolefins, polystyrene, polyvinyl chloride, polyamides, polyurethanes, polyester, ABS, ASA, polyphenylene oxides, vulcanized rubber, casein, silicone and silicone resins as well as their possible mixtures with one another.

It is also possible to use high molecular weight organic materials in dissolved form as film formers, for example boiled linseed oil, nitrocellulose, alkyd resins, phenolic resins, melamine/formaldehyde and urea/formaldehyde resins as well as acrylic resins.

Said high molecular weight organic compounds may be obtained singly or in admixture, for example in the form of granules, plastic materials, melts or in the form of solutions, in particular for the preparation of spinning solutions, paint systems, coating materials, inks or printing inks.

In a particularly preferred embodiment of this invention, the novel inventive polymer P2 are used for the mass coloration of polyvinyl chloride, polyamides and, especially, polyolefins such as polyethylene and polypropylene as well as for the preparation of paint systems, including powder coatings, inks, printing inks and coating colors.

Illustrative examples of preferred binders for paint systems are alkyd/melamine resin paints, acryl/melamine resin paints, cellulose acetate/cellulose butyrate paints and two-pack system lacquers based on acrylic resins which are crosslinkable with polyisocyanate.

According to observations made to date, the novel inventive polymer P2 can be added in any desired amount to the material to be colored, depending on the end use requirements. In the case of high molecular weight organic materials, for example, the pigments composed according to this invention can be used in an amount in the range from 0.01 to 40, preferably from 0.1 to 20 % by weight, based on the total weight of the colored high molecular weight organic material.

Hence, another embodiment of the present invention relates to a composition comprising

(a) 0.01 to 40, preferably 0.1 to 20% by weight, based on the total amount of (a) and (b), of inventive polymer P2, and

(b) 99.99 to 60, preferably 99.9 to 80% by weight, based on the total amount of (a) and (b) of a high molecular organic material, and

(c) if desired, customary additives such as fillers, paint auxiliaries, siccatives, plasticizers, UV-stabilizers, and/or additional pigments in effective amounts such as from 0.01 to 40, based on the total amount of (a) and (b).

The pigmenting of the high molecular weight organic materials with the novel inventive polymer P2 is usually effected by incorporating said novel inventive polymer P2, if desired in the form of masterbatches, in the high molecular weight organic materials using customary apparatus suitable to this end, such as extruders, roll mills, mixing or milling apparatus. The material thus treated is then normally brought into the desired final form by methods which are known per se, such as calandering, molding, extrusion molding, coating, casting, extruding, or by injection molding.

To produce non-brittle moldings or to diminish their brittleness, so-called plasticizers can be added to the high molecular weight substances prior to molding. Plasticizers may be, for example, esters of phosphoric acid, phthalic acid and sebacic acid. Said plasticizers may be added before, during or after pigmenting the high molecular weight substances with the inventive polymer P2 of this invention.

To obtain different shades, the novel inventive polymer P2 may advantageously be used in admixture with fillers, transparent and opaque white, colored and/or black pigments as well as customary luster pigments in the desired amount.

For the preparation of paints systems, coating materials, inks and printing inks, the corresponding high molecular weight organic substances, such as binders, synthetic resin dispersions etc. and the novel inventive polymer P2 are usually dispersed or dissolved together, if desired together with customary additives such as fillers, paint auxiliaries, siccatives, plasticizers and/or additional pigments, in a common solvent or mixture of solvents. This can be achieved by dispersing or dissolving the individual components by themselves, or also several components together, and only then bringing all components together, or by adding everything together at once.

For application in printing, all customary industrial printing processes can be employed, such as screen printing, rotogravure, bronze printing, flexographic printing and offset printing.

The inventive polymers P1 have the advantage that they exhibit a very narrow polydispersity.

Examples

The starting material used are derivatives of norbornene with an endo-exo ratio of 9:1. The norbornenes are synthesized using usual synthetic methods starting from Bicyclo[2.2.1]hept-5-ene-2 carboxylic acid methyl ester (obtained by Diels-Alder of cyclopentadiene with acrylic acid methyl ester).

Polymers are characterized by their GPC (showing less than 3% of monomers) and by elemental analysis.

$Cl_2[P(iPr)]_2Ru=CHPh$ is synthesized according to J. Am. Chem. Soc. 118 (1996) 100-110.

(A) Cholesteric polymer of the type P1, based on norbornene-ester

Example 1: 45.4 g (0.22 mol) of dicyclohexylcarbodiimide ("DCC") are added to a suspension of 30.4 g (0.22 mol) of bicyclo-[2.2.1]-hept-5-ene 2-carboxylic acid, 30.4g (0.22 mol) of 4-[6-(hydroxyhexyl)oxy] benzoic acid (as described in Macromolecules 1995, 28,

806) and 2.7 g (0.022 mol) dimethylaminopyridine ("DMAP") in 550 ml CH_2Cl_2. The mixture is stirred overnight at room temperature ("r.t.") under an atmosphere of nitrogen. The precipitated urea is filtered off and the resulting clear solution is extracted with a 5% b.w. aqueous solution of $NaHCO_3$. The aqueous phase is then acidified with conc. HCl and the precipitated product is filtered, washed with water and dried.

48.9 g (68.2%) of white powder are obtained.

Analysis:	C	H
calc.	70.37	7.31
exp.	70.36	7.47

Example 2: 5.23 g (0.044 mol) of thionyl chloride is added dropwise to a suspension of 14.34 g (0.04 mol) of the product obtained in example 1 in 50 ml of dried tetrahydrofurane ("THF") at r. t. The mixture is then heated to 50°C for 2 hours, at which point gas evolution has ceased. This crude mixture is added to a solution of 7.08 g (0.04 mol) 4-methacryloyl-amino-phenol (obtained by reaction of 4-aminophenol with methacryloyl anhydride according to J. Org. Chem. USSR 4 (1968) p. 802) and 8.9 g (0.088 mol) of triethylamine in 100 ml THF at 0°C. The reaction mixture is then heated at 55°C for 1.5 hours under an atmosphere of nitrogen. It is then poured on 1000 ml iced water. The precipitate is filtered, washed with water and dried. Recrystallization from EtOH affords 15.2 g (73%) of a white powder.

Analysis:	C	H	N
calc.	71.93	6.82	2.71
exp.	71.83	6.92	2.83

Example 3: 4.54 g (0.022 mol) of DCC are added to a suspension of 7.17 g (0.02 mol) of the product obtained in example 1, 7.73 g (0.02 mol) of cholesterol and 0.27 g (0.0022 mol) DMAP in 100 ml CH_2Cl_2. The mixture is stirred overnight at r. t. under an atmosphere of nitrogen. The precipitated urea is filtered off and the resulting clear solution is washed with a 5% b.w. aqueous solution of $NaHCO_3$, then with 0.1N HCl, followed by again a 5% b.w. aqueous solution of $NaHCO_3$, and finally with a saturated aqueous solution of NaCl. After drying over $MgSO_4$ the solvent is removed under a reduced atmosphere. The crude product is recrystallized from EtOH to give 5.93 g (41%) of a white powder.

Analysis:	C	H
calc.	79.29	9.70
exp.	79.25	9.83

Example 4: 93 mg (0.16 mmol) of $Cl_2[P(iPr)]_2Ru=CHPh$ is added to a rapidly stirred solution of 2.91 g (4 mmol) of the product obtained in example 3 and 2.07 g (4mmol) of the product obtained in example 2 in 80 ml dried CH_2Cl_2, and the mixture is stirred at r. t. for 6.5 hours under an atmosphere of nitrogen. Then 3 drops of ethylvinyl ether are added. After an additional 30 minutes, the solution is added dropwise to 1.2 liter of cold EtOH in a mixer. The precipitated polymer is filtered, washed with EtOH and dried in vacuo. 4.35 g (88%) of a white polymer are obtained.

GPC: M_n = 33104 g/mol M_w = 40199 g/mol PDI = 1.21

Analysis:	C	H	N
calc.	76.23	8.50	1.12
exp.	75.99	8.64	0.85

Thermotropic behaviour (determined using DSC and microscope): 90°C (T_g), 110°C - 170°C cholesteric phase, 170°C isotropic.

(B) Cholesteric polymer of the type P1, based on a norbornene-ether

Example 5: 4.14 g (0.03 mol) of 4-hydroxy-benzoic acid are added to a solution of 3.7 g (0.066 mol) of KOH and 10 mg crystals of KI in EtOH (60ml) and water (6ml). 9.41 g (0.033 mol) of bicyclo[2.2.1]hept-2-en-5-yl)methyl 6-bromohexyl ether (CA:151889-75-7) are added dropwise to this solution at r. t. and thereafter the mixture is heated at 75°C for 6 h. The mixture is poured on 500 ml of iced water. After acidification with 1N HCl the precipitated product is filtered, washed with water and dried.

The obtained crude product is dissolved in an aqueous solution of $NaHCO_3$ (5% b.w.) and then extracted with ethyl acetate. The separated aqueous phase is acidified with 10% aqueous HCl and the precipitated product is filtered, washed with water and dried. 6.11 g (59%) of a white powder are obtained.

Analysis:	C	H
calc.	73.23	8.19
exp.	72.92	8.08

Example 6: 2.27 g (0.011 mol) of DCC are added to a suspension of 3.44 g (0.01 mol) of the product obtained in example 5, 4.25 g (0.011 mol) of cholesterol and 0.13 g (0.0011 mol) of DMAP in 60 ml dried CH_2Cl_2. The mixture is stirred overnight at r. t. under an atmosphere of

nitrogen. The precipitated urea is filtered off and the resulting clear solution is washed with an aqueous 5% b.w. solution of $NaHCO_3$, then with 0.1N HCl, and afterwards with an aqueous 5% b.w. solution of $NaHCO_3$, and finally with a saturated aqueous solution of NaCl. After drying over $MgSO_4$ the solvent is removed under an atmosphere with a reduced pressure. The crude product is recrystallized from a mixture of EtOH and EtOAc (1:1 v/v) to give 4.7 g (66%) of a white powder.

Analysis:	C	H
calc.	80.85	10.18
exp.	80.88	10.18

Example 7: Example 6 is repeated with the exception that 4-methacryloylamino-phenol (4-Ph-N(H)-C(O)-C(Me)=CH_2) is used instead of cholesterol. Further, the crude product is recrystallized from a mixture of EtOH and water (2:1 v/v) to give a white powder in 60% yield.

Analysis:	C	H	N
calc.	73.93	7.41	2.78
exp.	73.27	7.40	2.83

Example 8: 23 mg (0.04 mmol) of $Cl_2[P(iPr)]_2Ru=CHPh$ is added to a rapidly stirred solution of 0.71 g (1 mmol) of the product obtained in example 6 and 0.50 g (1mmol) of the product obtained in example 7 in 20 ml dried CH_2Cl_2, and the mixture is stirred at r. t. for 5.5 hours under an atmosphere of nitrogen. Then 3 drops of ethylvinyl ether are added. After 30 minutes, the obtained solution is added dropwise to 345 ml of cold EtOH stirred in a mixer. The precipitated polymer is filtered, washed with EtOH and dried in vacuo. 1.08 g (89%) of a white polymer are obtained.

GPC: M_n = 23607 g/mol M_w = 29979 g/mol PDI = 1.27

GPC analyses shows less than 3% of monomers.

Analysis:	C	H	N
calc.	77.99	9.03	1.15
exp.	77.67	9.00	1.29

Thermotropic behaviour (determined using DSC and a microscope): 90°C (T_g), 110 - 175°C cholesteric phase, 175°C isotropic.

(C) Crosslinked, cholesteric polymer of the inventive type P2

Example 9: A mixture of 1g of the product obtained in example 4, 0.2 g of cholesterol 4-methacryloyloxy-benzoate, 0.1 g hexanediol dimethacrylate, 0.03 g of 2-methyl-1-(4-(methylthio)phenyl)-2-morpholino-propanone-1 (e.g. commercially available as IRGACURE®907, Ciba Specialty Chemicals Inc.), 0.005 g isopropenylthioxanthone (e.g. commercially available as QUANTACURE®ITX, Ciba Specialty Chemicals Inc.) and 500 ppm (related to the amount of polymer P1) p-tert butyl catechol is dissolved in 20 ml dichloromethane and then evaporated. The obtained homogeneous mixture is heated to 110°C giving a viscous liquid crystal. Then the liquid crystalline mixture is knife-coated on a polyester sheet maintained at the same temperature, in layer thickness of 6 µm. This layer is then irradiated for 30 seconds with UV-light and thus crosslinked three-dimensionally.

The material is removed mechanically by peeling off from the support using an ultrasonic bath. Milling of the material is then carried out in a air-jet mill.

Example 10: Example 9 is repeated with the difference, that 1g of the product obtained in example 8 is used.

Claims

1. Cholesteric polymer P1, obtainable by a ring-opening metathesis polymerization ("ROMP") of

(a) from 10 to 50 mol-% of a monomer with the formula I

$$Z(B_1)_y \qquad I$$

(b) from 90 to 50 mol-% of

(b1) from 0 to 100 mol-%, related to the sum of the amounts of (b1) and (b2), monomer with the formula II

$$Z(B_2)_y \qquad II$$

(b2) from 0 to 100 mol-%, related to the sum of (b1) and (b2), of a monomer with the formula III

$$Z(B_3)_y \qquad III$$

or a strained cyclic olefinic molecule,

wherein at least one of the monomers II or III is present,

the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%, wherein

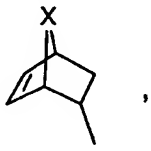
Z stands for A_1-A_2-A_3-A_4-A_5-A_6-A_7-, if y is 1, or, in case y is 2, for A_1-(A_2-A_3-A_4-A_5-A_6-A_7-)$_2$

B_1 stands for a chiral organic group,

B_2 stands for an organic crosslinkable group,

B_3 stands for an organic, non-chiral, non-crosslinkable group,

A_1 stands for a radical selected from the group consisting of



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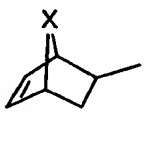

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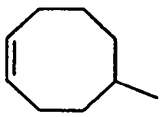
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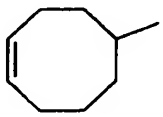
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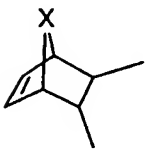
IVa IVb Va Vb



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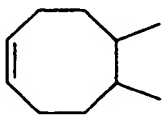


VIa VIb

whereby the exo- and the endo-isomers of the radicals IVa, IVb, and VIa are

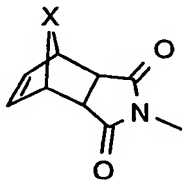
included, and whereby y is 1 in case A_1 is a monomer selected of IVa, IVb, Va, or Vb, or y is 2 in case A_1 is one of the biradicals VIa or VIb, and in which

X is selected from the group consisting of $-CH_2-$, -O- and -S-

A_2 is $-CH_2-$ or -C(O)-

A_3 is -O- or -NH-, or

A_1-A_2-A_3 stands for a radical of the formula VII



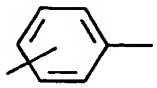
VII

A_4 is $-(CH_2)_{x1}-$ or $-[CH_2-CH_2-O-]_{x2}-CH_2-CH_2-$, wherein x_1 is an integer from 2 to 20, and x_2 is an integer from 1 to 6,

A_5 is one of the following radicals

-O-, -S-, -CO-O-, -O-CO-, -NH-CO-, -CO-NH-, -NH-

A_6 is



A_7 is -CO-O-, -O-CO-, -NH-CO-, -CO-NH-.

2. Three-dimensionally crosslinked and cholesteric polymer P2, whereby the crosslinkable, chiral polymer P1 as defined in claim 1 is further treated by crosslinking the crosslinkable groups B_2 in a photo polymerization reaction or thermally induced.

3. Compound $Z(B_1)_y$ as defined in claim 1.

4. Compound $Z(B_2)_y$ as defined in claim 1.

5. Compound $Z(B_3)_y$ as defined in claim 1.

6. Composition comprising from (a) 10 to 50 mol-% of compound $Z(B_1)_y$ as defined in claim 1and (b) from 90 to 50 mol-% of a mixture of (b1) from 0 to 100 mol-% of compound $Z(B_2)_y$ as defined in claim 1 and (b2) from 100 to 0 mol-% $Z(B_3)_y$ as defined in claim 1, wherein the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%.

7.Process for the preparation of polymer P1 according to claim 1, wherein the polymerized material is obtainable by copolymerization of at least two kinds of monomers, wherein one monomer is a chiral compound, characterized in
carrying out the copolymerization by a ring opening metathesis polymerization in the presence of a catalyst of
(a) from 10 to 50 mol-% of a monomer with the formula I

$$Z(B_1)_y \qquad I$$

(b) from 90 to 50 mol-% of
(b1) from 0 to 100 mol-%, related to the sum of the amounts of (b1) and (b2), monomer with the formula II

$$Z(B_2)_y \qquad II$$

(b2) from 0 to 100 mol-%, related to the sum of (b1) and (b2), of a monomer with the formula III

$$Z(B_3)_y \qquad III$$

or a strained cyclic olefinic molecule,
wherein at least one of the monomers II or III is present,
the mol-percentages of (a) and (b), and (b1) and (b2), resp., summing up to 100 mol-%, $Z(B_1)_y$, $Z(B_2)_y$, and $Z(B_3)_y$ being defined as in claim 1.

8. Process for the preparation of crosslinked polymer P2 as defined in claim 2, characterized in treating cholesteric polymer P1 as defined in claim 1 by crosslinking the crosslinkable groups B_2 in a photo polymerization reaction or thermally induced.

9. Use of polymer P2 as defined in claims 1 and 2 as pigments for coloring high molecular weight organic materials, glasses, ceramic products, for formulations in decorative cosmetics, for the preparation of inks, printing inks, paint systems, in particular automotive paints and dispersion colors.

10. Composition comprising
(a) 0.01 to 40% by weight, based on the total amount of (a) and (b), of polymer P2 according to claim 2, and
(b) 99.99 to 60% by weight, based on the total amount of (a) and (b) of a high molecular organic material, and
(c) if desired, customary additives such as fillers, paint auxiliaries, siccatives, plasticizers, UV-stabilizers, and/or additional pigments in effective amounts.

INTERNATIONAL SEARCH REPORT

Int[illegible]ional Application No
PCT/EP 99/00281

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/08 C09K19/38 C07C233/20 C07C69/74 C07J9/00
C09B67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C09K C07C C09B C07J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PUGH C: "LIVING RING OPENING METATHESIS POLYMERIZATION OF MESOGENIC NORBORNENE DERIVATIVES" MACROMOLECULAR SYMPOSIA, vol. 77, 1 January 1994 (1994-01-01), pages 325-337, XP000433249 ---	
A	CHO I ET AL: "CHARACTERISTICS OF LIQUID-CRYSTALLINE CHOLESTERYL AND CYANOBIPHENYL SIDE CHAINS PENDENT TO TRANS-POLYPENTENAMER" MACROMOLECULAR: RAPID COMMUNICATIONS, vol. 18, no. 1, January 1997 (1997-01), pages 45-51, XP000636342 --- -/--	

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 July 1999	13/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stienon, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/00281

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WINKLER B ET AL: "A NOVEL SIDE-CHAIN LIQUID CRYSTAL POLYMER OF 5-SUBSTITUTED CIS-CYCLOOCTENE VIA RING-OPENING METATHESIS POLYMERISATION" MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 198, no. 5, May 1997 (1997-05), pages 1417-1425, XP000657577	

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